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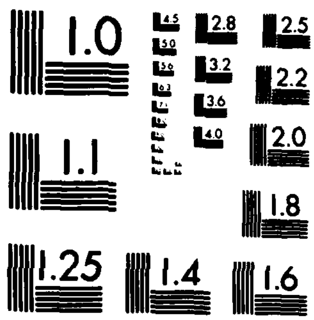

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TECHNICAL REPORT NO. 15

Observation of a Reversible Adsorbed Redox Couple Using Surface-Enhanced Raman Scattering: Pentaamminepyridineosmium(III)/(II) at Silver Electrodes

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Surface-enhanced Raman scattering (SERS) has been observed for pentaamminepyridineosmium(III) adsorbed at a silver electrode as a function of electrode potential in order to examine the molecular vibrational changes accompanying electron transfer involving a simple surface-bound redox couple. Noticeable alterations in the intensity and frequency of several vibrational bands involving osmium-ligand and pyridine ring modes were observed as the electrode potential was made more negative which are consistent with a variation of the osmium oxidation state from III to II. The effective formal

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) potential for the adsorbed Os(III)/(II) couple determined from SERS, ca -630 mV vs sce, is in reasonable agreement with that obtained from rapid cyclic voltammetry, illustrating the value of SERS for monitoring electron-transfer processes at metal surfaces.

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OBSERVATION OF A REVERSIBLE ADSORBED REDOX COUPLE USING SURFACE-ENHANCED RAMAN SCATTERING: PENTAAMMINEPYRIDINEOSMIUM(III)/(II) AT SILVER ELECTRODES

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We wish to report Surface-Enhanced Raman Scattering (SERS) for pentaammine-pyridineosmium (III) and (II) adsorbed on a silver electrode. This appears to be the first employment of SERS for following electron transfer with a simple adsorbed redox couple. We have been examining SERS of structurally simple adsorbates under electrochemically characterized conditions.[1-3] One objective is to relate SERS measurements to electrochemical phenomena; despite the recent proliferation of SERS studies,[4] few investigations of this type have been reported. Pentaammmineosmium compounds[5] are particularly suitable for the present work since they are substitutionally inert in both (*III*) and (*II*) oxidation states and have formal potentials compatible with the potential range (ca 0 to -1.0 V vs. the saturated calomel electrode, sce) available at silver electrodes. Adsorbed redox couples having nitrogen heterocycle bridging groups constitute direct heterogeneous analogs of the much-studied intramolecular redox systems in homogeneous solution.

Conventional conditions for the optimal appearance of SERS were employed,[3,4a] involving roughening the silver electrode by means of oxidation-reduction cycles using 0.1 $\underline{M}$ NaCl or NaBr supporting electrolytes, also containing 0.1 - 1.0 m$\underline{M}$ $[Os(NH_3)_5py]Cl_3 \cdot H_2O$[5] (py = pyridine) and 0.1 $\underline{M}$ HCl.[6] Raman excitation employed either 647 or 514 nm laser irradiation. All potentials quoted are versus the sce; other experimental details are given elsewhere.[3,7]

SERS spectra were recorded over the frequency range 140-3500 cm^{-1} in 100 mV potential increments from -150 to -850 mV. A summary of some representative vibrational bands is given in Table I; typical spectra as a function of potential are shown in Figure 1.[8] Assignments are based on comparisons with spectra for structurally similar pyridine and ammine complexes[9] and from selective deuteration of the pyridine or ammonia ligands.[3] Aside from the appearance of the halide surface modes at 235 and 180 cm^{-1} for chloride and bromide electrolytes, respectively, the spectral frequencies were essentially identical in both media. (This supports the assignment of the 291 and 267 cm^{-1} vibrations to osmium - pyridine stretching rather than to surface-ligand modes.) At potentials positive of -500 mV, the SERS vibrational frequencies for adsorbed $Os^{III}(NH_3)_5py$ are closely similar to those seen for the bulk Raman and infrared spectra (Table I). However, notable spectral changes occurred as the potential was made more negative. In particular, the intensities of the Os-py stretching (291 cm^{-1}), Os-NH_3 stretching (494 cm^{-1}), and symmetric ring breathing (1020 cm^{-1}) modes decreased sharply between -500 and -700 mV, being replaced by corresponding peaks having 20-30 cm^{-1} lower frequencies. These changes could be entirely reversed by returning the potential to less negative values. In contrast, adsorbed pyridine shows little change ($\lesssim$ 2 cm^{-1}) in SERS vibrational frequencies and only mild intensity changes over this potential region[10] (Table I).

These spectral changes are consistent with a one-electron reduction of the adsorbed Os(III) complex to the corresponding Os(II) species. Metal-ligand stretching modes commonly exhibit such a dependence upon oxidation state.[9] Of the various pyridine vibrations, the symmetric ring breathing mode is known to be sensitive to the coordinating environment, exhibiting decreasing frequencies as the electron density on the pyridine ring increases.[11] This latter effect is expected to be especially important for $Os^{II}(NH_3)_5py$ on account of the high degree of π-bonding.[5,12] Indeed, an almost identical frequency shift in this mode is seen for the infrared spectra of the bulk Os(III) and Os(II) complexes (Table I).

Using rapid scan cyclic voltammetry (50-100 V sec^{-1}) and very dilute $Os(NH_3)_5py^{3+}$ concentrations ($\sim$50 $\mu\underline{M}$),[13] the formal potential of the adsorbed

Os(III)/(II) couple, E_f^a, was found to be -670 mV in 0.1 $\underline{M}$ HCl at roughened silver, (cf the formal potential for the bulk couple, E_f^b = -655 mV). Moderate adsorption ($\sim$ 3 to 4 x 10^{-11} mol. cm^{-2}) was indicated by the charge underneath the almost symmetric cyclic voltammograms. Formal potentials, E_f^a, were also determined from the SERS intensity-potential data. Figure 2 shows the potential dependence of the normalized integrated intensities, of the 1020 cm^{-1} and 992 cm^{-1} SERS ring breathing modes in the vicinity of E_f^a. Assuming the intensities are proportional to the corresponding surface concentrations, a Nernstian treatment[3] gave values of E_f^a (-630 ± 10 mV) similar to those determined electrochemically.

The appearance of SERS signals for the present system is in itself noteworthy since coordinated pyridine is unable to bind to the surface via the nitrogen lone pair. Such surface coordination is often regarded as a prerequisite for the appearance of SERS for adsorbed pyridine.[4a] Adsorption of the coordinated pyridine is likely to occur edgewise via a C=C bond;[14] the alternative flat orientation will be sterically hindered by the presence of the coordinated pentaammineosmium. Direct metal-pyridine bonding is also consistent with the excellent mediating properties of coordinated pyridine for pentaamminecobalt(III) reduction at metal surfaces.[15] Nevertheless, the adsorbate-electrode interactions are presumably weak, as evidenced by the similarity of E_f^a and E_f^b, and the vibrational frequencies of $Os(NH_3)_5py$(III)/(II) at the surface and in bulk media. SERS of osmium and ruthenium complexes containing coordinated pyrazine and 4,4'-bipyridine ligands that are able to bind to the surface via the exposed nitrogen, thereby yielding stronger adsorbate-surface interactions, will be described elsewhere.[3]

The present results illustrate the potential of SERS for monitoring heterogeneous electron-transfer processes, and suggest that adsorbates bound to SERS-active sites are energetically similar to those observed by conventional electrochemistry.

Acknowledgments

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8. Essentially identical vibrational frequencies were obtained with supporting electrolytes containing 0.1 M chloride or bromide. However, the latter electrolyte was preferred for most measurements as it yielded markedly more intense SERS spectra at the more negative potentials (∿ -600 mV) of particular interest here.[3]

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TABLE I

Summary of Representative Vibrational Frequencies (cm^{-1}) observed for $Os^{III}(NH_3)_5py$, $Os^{II}(NH_3)_5py$, and pyridine at silver electrodes and in bulk media.[a]

$Os(NH_3)_5py$					Pyridine	Assignment[h]
IR[b]	IR[b]	Raman[c]	SERS[d]		SERS[g]	
Os(III)	Os(II)	Os(III)	-150mV	-750mV		
-	-	-	291w	267m	-	Os-py stretch
-	-	501w	494w	468m	-	Os-NH_3 stretch
-	-	654w	653m	648s	625w[e], 623[f]	in-plane ring deformation
1022m	990m	1020s	1020vs	992s	1007vs[e], 1007[f]	symmetric ring breathing
1055w	1055w	-	1050m	1053s	1035s[e], 1035[f]	trigonal ring breathing

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak

[b] Infrared data obtained using $Os(NH_3)_5py{\cdot}I_3$ and $Os(NH_3)_5py{\cdot}I_2$ in CsI pellets.

[c] Normal Raman data obtained using $Os(NH_3)_5py{\cdot}Cl_3$ in KBr pellets.

[d] Surface-enhanced Raman vibrational modes for electrochemically roughened silver electrode in 0.1 M NaBr + 0.1 M HCl + 0.1 mM $Os(NH_3)_5py^{3+}$ at indicated potentials versus sce.

[e] From this work, for 10 mM pyridine in 0.1 M NaBr.

[f] From ref 10, for 50 mM pyridine in 0.1 M KCl.

[g] Frequencies were potential independent (± 2 cm^{-1}) from -150 to -750 mV.

[h] See text for details.

Figure Captions

Figure 1: Potential-dependent SERS of $Os(NH_3)_5py(III)/(II)$ at roughened silver; 514.5 nm excitation, 100 mW incident power, scan speed 1 cm^{-1} sec^{-1}, time constant 1 sec, resolution 4 cm^{-1}. Solution contained 0.1 m<u>M</u> $Os(NH_3)_5py^{3+}$ in 0.1 <u>M</u> NaBr + 0.1 <u>M</u> HCl. (291 cm^{-1} peak seen more clearly in x5 top spectrum in C).

Figure 2: Normalized intensity of the symmetric ring breathing mode as a function of electrode potential. Osmium oxidation states are indicated. Data as in Fig 1.

FIG 1

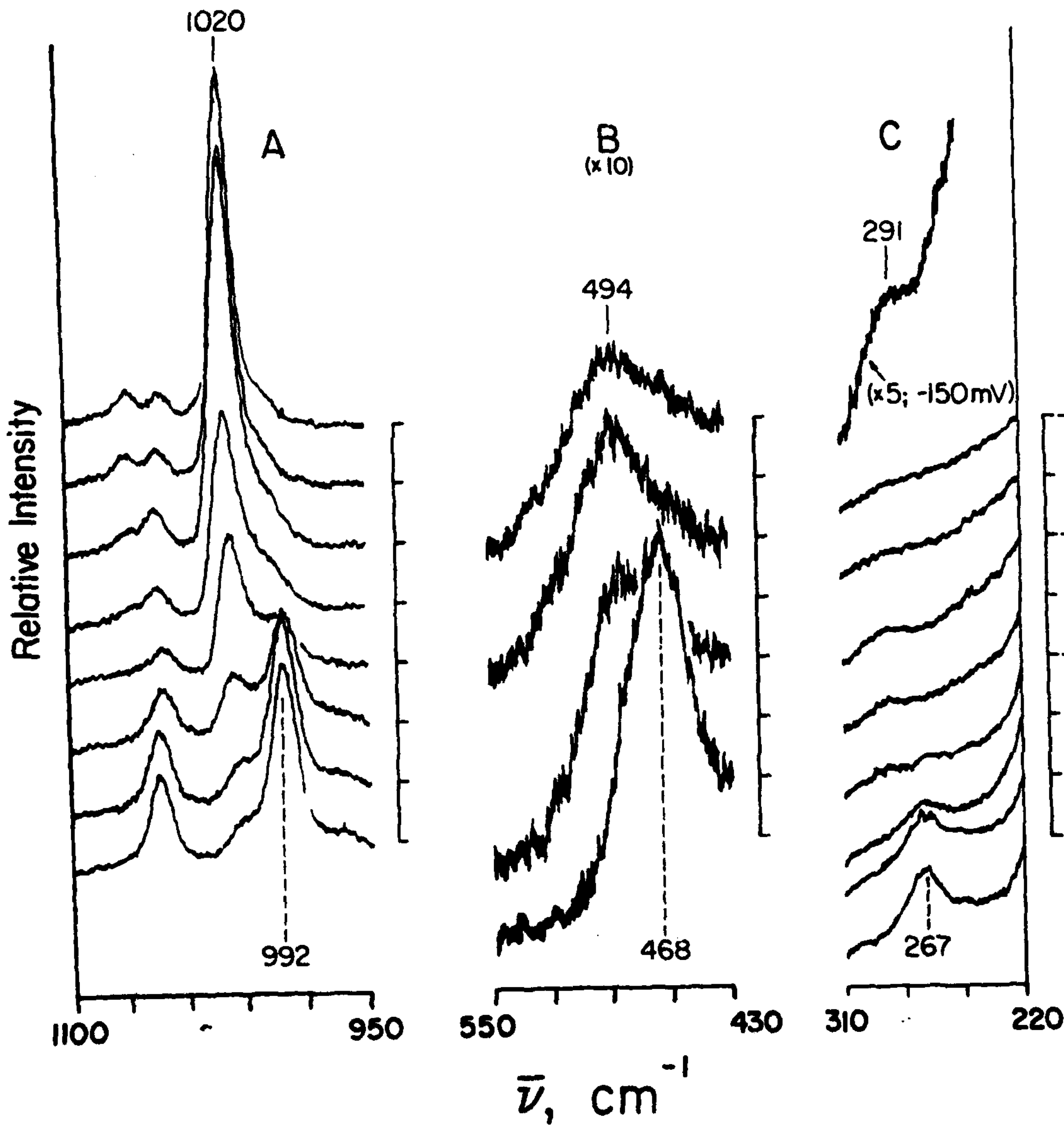
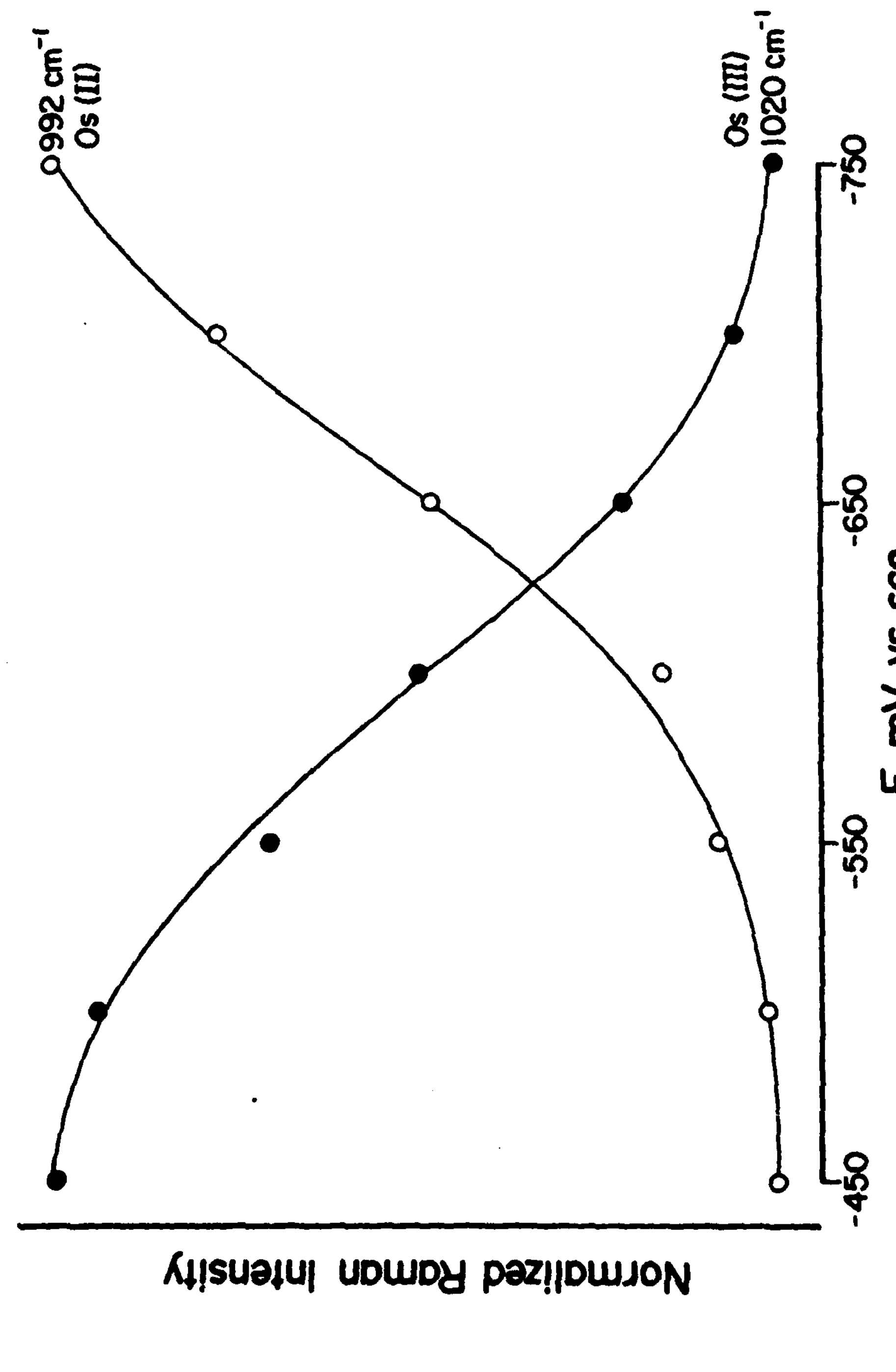

1020
A
B
(×10)
C
291
494
(×5; -150mV)
Relative Intensity
-150
-350
-550
-750
E, mV vs. sce
992
468
267
1100
950
550
430
310
220
$\bar{\nu}$, cm^{-1}

FIG 2


992 cm⁻¹
Os (II)
Os (III)
1020 cm⁻¹
-750
-650
-550
-450
E, mV vs sce
Normalized Raman Intensity

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